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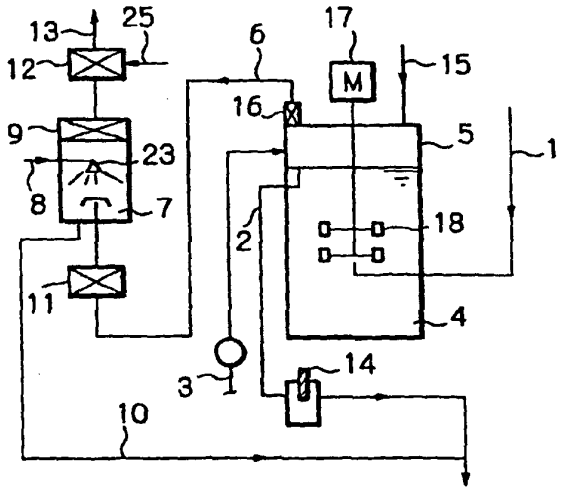
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(54) METHOD AND APPARATUS FOR PROCESSING EXHAUST GAS OF SEMICONDUCTOR FABRICATION

(57) A process and an apparatus for treating exhaust gases, comprising an aeration stirring tank (5) employing an aqueous alkaline liquid, and a gas-liquid contact device (7) and/or a packed column (11). The apparatus can remove at a posterior stage harmful gases failed to be removed by the aeration stirring tank, for example, water-soluble organic compounds such as ethanol, halogenated silicon compounds such as $SiCl_4$, and halogen gases such as F_2 and Cl_2. It is particularly suitable for purifying exhaust gases discharged from a semiconductor production device.

Fig.3



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[0010] In the present invention, the above removal step preferably comprises a step of allowing the gases discharged from the aeration stirring tank to come into contact with an aqueous liquid. Or, the above removal step preferably comprises a step of introducing the gases which have been discharged from the aeration stirring tank into a packed column filled with treating agent. Alternatively, the above removing process preferably comprises a step of allowing the gases discharged from the aeration stirring tank to come into contact with an aqueous liquid, and a step of introducing the gases discharged from the aeration stirring tank into a packed column filled with a treating agent.

[0011] It is preferable that the above aqueous alkaline liquid is an aqueous solution containing no alkaline metal element and that the pH of said aqueous solution is from 7.1 to 10.

[0012] In addition, it is preferable that the gases discharged from the aeration stirring tank are transferred by a gas transfer device. As the gas transfer device, a gas suction device to be installed at the downstream of a gas-liquid contact device or a packed column can be exemplified. However, a fan may be installed as the gas transfer device at the upstream of the gas-liquid contact device or the packed column.

[0013] The process preferably comprises further a step of discharging exhaust gases from the semiconductor production apparatus, said exhaust gases being introduced into the above aqueous alkaline liquid in the above introduction step.

[0014] According to another aspect of the present invention, an apparatus for treating exhaust gases is provided, which comprises

an aeration stirring tank for introducing exhaust gases into an aqueous alkaline liquid while stirring the aqueous alkaline liquid; and

at least one of a gas-liquid contact device for allowing gases discharged from said aeration stirring device to come into contact with the aqueous liquid and a packed column filled with an agent for passing gases discharged from said aeration stirring device.

[0015] In the present invention, the apparatus preferably comprises said gas-liquid contact device. Or, in the present invention, the apparatus preferably has said packed column. Or the apparatus preferably comprises said gas-liquid contact device and said packed column.

[0016] In addition, the apparatus preferably comprises a gas transfer device for transferring gases which have passed through the aeration stirring tank.

[0017] Moreover, the apparatus preferably comprises a passage for introducing exhaust gases discharged from the semiconductor production apparatus into said aeration stirring tank.

[0018] According to the present invention, acid gases such as HCl and HF, organic silicon compounds such as tetraethoxy silicon, and inorganic halogen compounds such as BCl_3 and $SiCl_4$ can be removed in the aeration stirring tank.

[0019] Besides, in the present invention, harmful gases which have failed to be removed by the aeration stirring tank, for example, alkaline gases such as ammonia and amine, water-soluble organic compounds such as ethanol and acetoaldehyde, halogenated silicon compounds such as $SiCl_4$, and halogen gases such as F_2 and Cl_2 can be removed by the gas-liquid contact device or the packed column at a posterior stage. Very small amounts of acid gases such as HCl and HF may pass through the aqueous alkaline liquid at times, and such very small amounts of acid gases can also be removed at a posterior stage.

[0020] The gas-liquid contact device is particularly suitable for removing water-soluble organic compounds, acid gases and alkaline gases. On the other hand, the packed column filled with a treating agent is particularly suitable for removing halogenated silicon compounds and halogen gases.

[0021] The present invention does not intend to remove organic fluorine compounds such as CF_4, CHF_3 and C_2F_6. This is because these organic fluorine compounds are chemically stable and do not significantly affect semiconductor production.

[0022] According to the present invention, in the process for treating exhaust gases by allowing semiconductor production exhaust gases to come into contact with an alkaline solution, thereby removing harmful components, it is possible to conduct the bringing into contact of said exhaust gases with the alkaline solution in the aeration stirring tank, and allow the gases after contact to come into further contact with water, as well as, bring these gases into contact with the solution by gas suction at a posterior stage.

[0023] Moreover, according to the present invention, in the apparatus for treating exhaust gases by allowing semiconductor production exhaust gases to come into contact with an alkaline solution, thereby removing harmful components, it is possible to employ an aeration stirring tank for allowing the exhaust gases to come into contact with the alkaline solution and a gas-liquid contact device for allowing exhaust gases from the stirring tank to come into contact with water, and further install a gas suction device for sucking gases at a stage posterior to these devices.

[0024] In the present invention, exhaust gases can be contact with treating agent in a packed column filled brought into with the agent; in addition, the pH of said alkaline solution is preferably adjusted to from 7.1 to 10, in particular, from

a high speed, a gas is introduced by the direct pipe 19 from immediately below the stirring blade, and the gas is turned into fine foam by the shear force of the stirring blade to disperse the liquid; moreover, the stirring blade is preferably provided in two steps upward and downward and rotated at a high speed with a view to increasing the retention time of the foam in the liquid and the shear force of the stirring blade.

[0036] Fig. 4 (b) shows a device wherein the stirring blade 18 (disc turbine blade), which is directly connected to the motor 17, and has several right-angled turbine blades attached to the disc-like circumference, is rotated in a liquid at a high speed, a gas in the form of fine bubbles is introduced by the porous pipe 21 from right below the stirring blade, and the gas is divided into finer foam by the shear force of the stirring blade provided right overhead to disperse the liquid. 20 shows a baffle.

[0037] The reason why the aeration stirring tank is employed in this way in the present invention will be described hereunder.

[0038] In the case of treating a high-concentration acid gas with an alkaline liquid in a liquid dispersion type wet absorption device such as a packed column generally and widely employed, a mist containing a salt produced by a neutralization reaction is formed. For example, when a HCl-containing gas is treated with ammonia water as a neutralization liquid, a mist containing NH_4Cl is formed. Besides, when sodium hydroxide is employed as a neutralization liquid, a mist containing NaCl is formed. When BCl_3 and SiF_4 are wet-treated, a mist containing B_2O_3 or SiO_2 which is a hydrolyzed product thereof is formed. Since these products may be deposited at a stage posterior to the treatment device and cause trouble such as blocking, it is necessary to prevent their formation.

[0039] It is guessed that these mists are produced by a reaction of treatment object components with fine particles of a washing liquid present in the absorption device and components volatilizing from the washing liquid (for example, a water molecule and an ammonia molecule). In general, while the diffusion coefficient of a gaseous molecule is of the order of 10^{-5} m^2/sec, the diffusion coefficient of these mists is said to be of the order of 10^{-3} to 10^{-11} m^2/sec, and thus, the diffusion rate is extremely slow.

[0040] In general, in a wet absorption device, as a result of treating object components dissolved in a liquid, the concentration of the gas phase at the gas-liquid interface decreases, and a concentration gradient occurs in the gas phase nearby. The treatment object components are dispersed and transported by this concentration gradient, and the dissolution of the treatment object components into the liquid is accelerated. The transport amount by diffusion is in proportion to the diffusion coefficient of the treatment object components. However, since the diffusion coefficient of the mists are extraordinarily small in comparison with that of a gaseous molecule as described above, the transport amount by diffusion becomes extraordinarily small. Therefore, the dissolution rate of mist components into a liquid film is slow and sufficient removal performance cannot be obtained.

[0041] Hence, in order to sufficiently remove the resultant mists by the dissolution thereof into the liquid, it is necessary to accelerate the dissolution of the mists through a mechanism other than diffusion transport.

[0042] In the present invention, a device capable of obtaining a high removal performance is obtained by accelerating the renewal of a gas-liquid interface by finely dividing foam in a liquid by a stirring blade and accelerating dissolution by maintaining the mist concentration high in the gas phase at the gas-liquid interface.

[0043] Subsequently, since the gas 6 coming out of the aeration stirring tank 5 contains mainly treatment object components which have been failed to be removed, or ammonia and amine in the case of employing a volatile alkaline liquid, it is allowed to come into contact with water 8 in a suitable gas-liquid contact device 7, and then droplets are removed by the demister 9.

[0044] As the gas-liquid contact device to be employed here, any appropriate known device can be employed, and for example, those described in Fig. 5 (a) and Fig. 5 (b) may be employed.

[0045] Fig. 5 (a) shows a packed column filled with a Raschig ring 22 in the inside thereof. Water 8 is sprayed from the upper part of the Raschig ring 22 onto the top of the filling, and the gas 6 is subjected to gas-liquid contact when it passes the filling zone.

[0046] Fig. 5 (b) shows a shower column equipped inside thereof with a spray nozzle 23. Water 8 is sprayed in the form of a water film from the tip of the spray nozzle 23, and the gas is subjected to gas-liquid contact when it passes through the water film.

[0047] Water after subjected to the gas-liquid contact is discharged from the drainage pipe 10. Here, most of ammonia and amine are absorbed, and their concentration is reduced to an amount which is lower than the acceptable concentration for working circumstances.

[0048] The treated gas passes the suction device 12 and is discharged from the device as shown line 13. As an example of the suction device 12 an ejector type suction device can be employed, wherein high-pressure air or water is jetted from a nozzle and by suction force generated there, the pressure of the secondary side becomes negative; a fan and a water seal pump can also be employed.

[0049] The suction device is not an indispensable device, and the pressure of the primary side may be made positive instead of the pressure of the secondary side being made negative. For example, it is possible to provide a fan on the primary side and introduce a gas.

Example 1

[0062] Employing a treating apparatus shown in Fig. 2, an exhaust gas discharged from an Al etching device for semiconductor production was treated. The flow rate of the semiconductor exhaust gas was 40 l/min.

[0063] The semiconductor exhaust gas 1 was, first of all, introduced into an aeration stirring tank 5 filled with water 4, the pH of which was adjusted to from 8.5 to 9.5 with the addition use of ammonia water 3. The introduced gas was then finely divided by a stirring blade 18 rotated with a motor 17 and came into contact with water 4. The rotation speed of the stirring blade 18 was set at 600 rpm. In order to prevent products from accumulating in the water 4, water 15 was introduced at a rate of 3 l/min into the aeration stirring tank, and the same amount of a blow-down drain 2 was drained. The pH of the blow-down drain was constantly monitored by a pH electrode 14, and the ammonia water 3 was injected when the pH was below 9.

[0064] The aeration stirring tank outlet gas 6 coming out of the aeration stirring tank was passed through water shower 7 sprayed from a spray nozzle 23 at a flow rate of 5 l/min, and allowed to come into contact with water 8. Water after contact was discharged as a water shower drain 10. A demister 9 was provided at the outlet of the water shower in order to prevent the sprayed water from the spray nozzle 23 from flying into subsequent stages. The water shower outlet gas 24 coming out of the water shower was introduced into the packed column 11 which had been filled with 10 l of an anion exchange resin. The packed column outlet gas coming out of the packed column was introduced into an air ejector 12 to be driven by air 25 and discharged as a treated gas 13. The amount of air 25 introduced was determined to 40 l/min.

[0065] The gas treatment was performed in an apparatus having the above constitution, and the semiconductor exhaust gas 1, the aeration stirring tank outlet gas 6, the water shower outlet gas 24 and the treated gas 13 were analyzed. The results are shown in Table 1.

[0066] For comparison, the same exhaust gas was treated by employing ammonia water for adjusting a pH, and a packed column type scrubber a Raschig ring as a filler. Other conditions were the same as those in Example. The results of the treatment are shown in Table.

Table 1

	1)	2)	3)	4)	5)
BCl_3 (unit: ppm)	5000	< 1	< 1	< 1	< 1
Cl_2 (unit: ppm)	3000	2	2	< 0.5	3
$AlCl_3$ (unit: ppm)	10	< 1	< 1	< 1	< 1
NH_3 (unit: ppm)	< 1	50	< 1	< 1	
B_2O_3 (mg/m^3)	< 1	15	10	< 1	300
NH_4Cl (mg/m^3)	< 1	20	15	< 1	400

1) Semiconductor exhaust gas 1
2) Aeration stirring tank outlet gas 6
3) Water shower outlet gas 24
4) Treated gas 13
5) Packed column type scrubber

[0067] BCl_3, Cl_2 and $AlCl_3$ contained in the exhaust gas were treated at each stage, and thereby the concentration of each of these components in the treated gas was below a detection limit. Besides, components such as NH_3, B_2O_3 and NH_4Cl generated during the process of the treatment were treated by the water shower and the adsorption column to lower the concentration below their detection limits.

[0068] In the case where the treatment was performed by the packed column scrubber, B_2O_3 and NH_4Cl leaked by 300 mg/m^3 and 400 mg/m^3, respectively. In contrast, in the case of treatment by the aeration stirring tank, the leak concentrations of B_2O and NH_4Cl were 15 mg/m^3 and 20 mg/m^3, respectively, which are lower by one or more orders as compared with the case of the packed column scrubber.

Example 2

[0069] The treatment was conducted continuously for one month, and no trouble such as blocking in the apparatus due to solids contained in the semiconductor exhaust gas and heat release occurred. Moreover, the inside of the duct

Table 3

	1)	2)	3)	4)
BCl_3 (unit: ppm)	5000	< 1	< 1	< 1
Cl_2 (unit: ppm)	3000	2	< 0.5	< 0.5
$AlCl_3$ (unit: ppm)	10	< 1	< 1	< 1
NH_3 (unit: ppm)	< 1	80	100	< 1
B_2O_3 (unit: ppm)	< 1	40	10	< 1
NH_4Cl (mg/m^3)	< 1	80	15	< 1

1) Semiconductor exhaust gas 1
2) Aeration stirring tank outlet gas 6
3) Packed column outlet gas
4) Treated gas 13

[0075] BCl_3, Cl_2 and $AlCl_3$ contained in the exhaust gas were treated at each stage, and thereby the concentration of each of these components in the treated gas was reduced to a level lower than their detectable limits. Besides, components such as NH_3, B_2O_3 and NH_4Cl generated during the process of the treatment were treated by the water shower and the packed column to lower the concentration below their detection limits.

[0076] According to the present invention, the following effects can be achieved.

(1) In the above treatment process, a reaction product of treatment object components with water or an alkaline liquid is prevented from leaking at subsequent stages by employing an aeration stirring tank at an initial stage, thereby troubles caused by the product can be reduced.
(2) The treating performance can be compared to that of a dry type treatment if a packed column is fitted at a subsequent stage.
(3) Since the majority of treatment object components are removed at a wet treatment stage even if a packed column is fitted, the packed column has a long-life and may be of a very small size. Therefore, time required for the replacement and running cost can remarkably be reduced.
(4) Since the amount of harmful materials to be condensed in the packed column is small, troubles such as heat generation do not occur easily, and the stabilization of the used agent presents no difficulties.
(5) Although the gas inlet pressure of the aeration stirring tank becomes positive, the load of a vacuum pump equipped at its upstream can be reduced if a suction device is placed at a subsequent stage.

Claims

1. A process for treating exhaust gases, comprising

 a step of introducing exhaust gases into an aqueous alkaline liquid in an aeration stirring tank while stirring the liquid, and
 a step of removing harmful gases from the gases discharged from the aeration stirring tank.

2. A process for treating exhaust gases according to Claim 1, wherein said removal step comprises a process of allowing the gases discharged from the aeration stirring tank to come into contact with an aqueous liquid.

3. A process for treating exhaust gases according to Claim 1, wherein said removing step comprises a step of introducing the gases discharged from the aeration stirring tank into a packed column filled with an agent.

4. A process for treating exhaust gases according to Claim 1, wherein said removing step comprises a step of allowing the gases discharged from the aeration stirring tank to come into contact with an aqueous liquid, and a step of introducing the gases discharged from the aeration stirring tank into a packed column filled with an agent.

5. A process for treating exhaust gases according to any one of Claims 1 to 4, wherein said aqueous alkaline liquid is an aqueous solution containing no alkaline metal element and the pH of said aqueous solution is from 7.1 to 10.

Fig.1

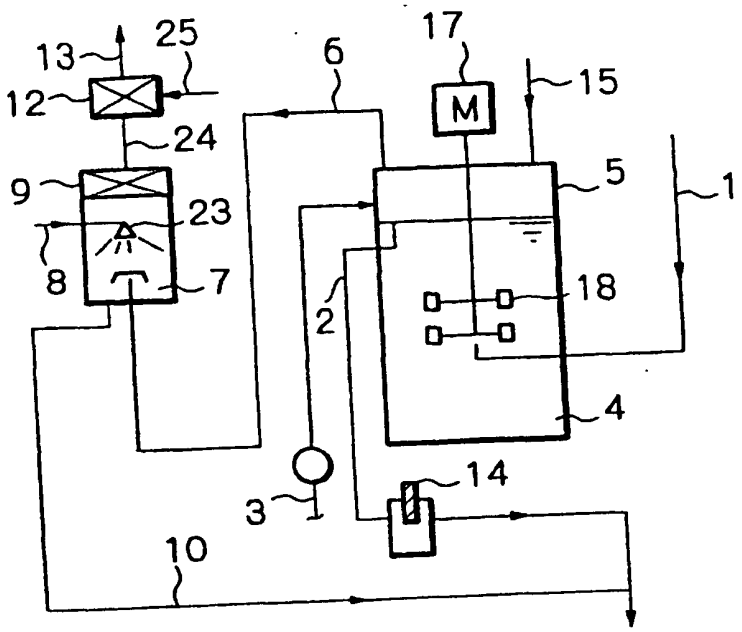

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Fig.2

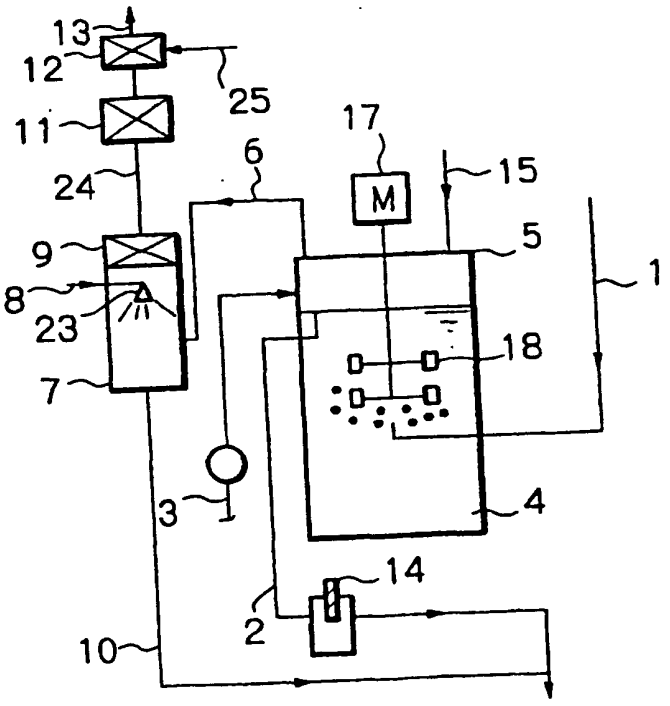

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Fig.5(a)

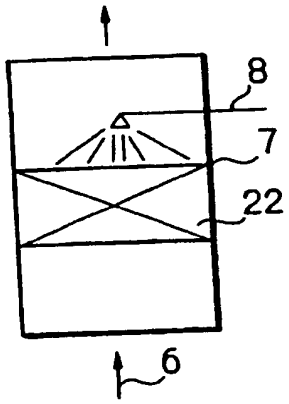
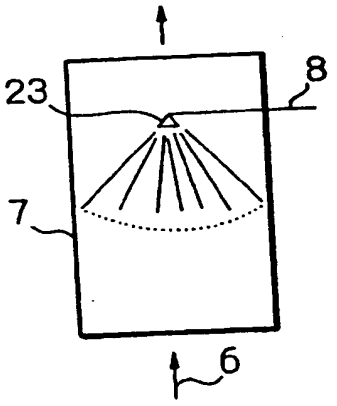


Fig.5(b)



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP98/04666

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl[6] B01D53/75, B01D53/78

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl[6] B01D53/34, B01D53/75, B01D53/78

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1922-1996 Toroku Jitsuyo Shinan Koho 1994-1999
Kokai Jitsuyo Shinan Koho 1971-1999 Jitsuyo Shinan Toroku Koho 1996-1999

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP, 3-242215, A (Iwatani & Co., Ltd.), 29 October, 1991 (29. 10. 91), Page 2, upper left column, lines 2 to 18 (Family: none)	1, 3, 7, 8, 10, 13 6, 12
X Y	JP, 8-309147, A (Kobe Steel, Ltd.), 26 November, 1996 (26. 11. 96), Claims 5, 8, 9 ; Fig. 5 (Family: none)	1-4, 8-11 6, 12
X	Microfilm of Japanese Utility Model Application No. 118088/1974 (Laid-open No. 44744/1976) (Kajima Corp.), 30 September, 1974 (30. 09. 74), Page 4, line 11 to page 5, line 2 ; Fig. 1 (Family: none)	1, 3, 5-8, 10, 12
X Y	JP, 8-57254, A (Masataka Ishikawa), 5 March, 1996 (05. 03. 96), Par. Nos. [0018], [0019] ; Fig. 1 (Family: none)	1, 2, 8, 9 3, 4, 6, 10-12

[X] Further documents are listed in the continuation of Box C. [] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
8 January, 1999 (08. 01. 99)	19 January, 1999 (19. 01. 99)
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